(PEG m-values) for EG and a wide range of PEG chain lengths. EG and small PEG oligomers are destabilizing to hairpin and duplex; with increasing PEG size this destabilization decreases so that large PEGs are only slightly destabilizing to the hairpin and stabilizing to the duplex. We conclude that contributions of preferential interactions to PEG m-values increase in proportion to the product of the amount of DNA surface exposed on melting and the amount of surface of PEG accessible to, and therefore able to interact with, this DNA surface. We further conclude that the large stabilizing effect of crowding on the duplex is due to the assembly of two reactants into product while the crowding effect on the hairpin is much weaker because hairpin folding involves only a small change in shape and not assembly of multiple reactants. Finally, we examine the concentrated PEG solution regime where PEG chains interpenetrate.

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300-Pos Board B100

Volumetric Characterization of Sodium-Induced G-Tetraplex Formation

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Oligodeoxyribonucleotides containing telomeric sequences form unique tetrahelical structures in which guanine repeats from different segments of the oligonucleotide hydrogen bond with each other in an arrangement called a guanine tetrad and they coordinate monovalent cations. The secondary structure of these sequences in aqueous solution varies depending on the ionic species present in solution. Since the discovery of their functional importance in eukaryotic chromosomes various sequences and their thermodynamics properties have been extensively studied. We have characterized the volumetric properties of single-strand to quadruplex transition of the human telomeric sequence by pressure perturbation calorimetry, high precision densimetry, ultrasonic velocimetry and high pressure UV melting. The methods yield consistent results providing insight into the packing and hydration properties of the tetraplex. This is, to our knowledge, the first time all of these techniques have been applied to the same system.

301-Pos Board B101

Single-Stranded DNA Oligomers may have a Molten Globule-Like Conformation in Solution

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The electrophoretic mobility of any analyte, including DNA, is the quotient of its net charge divided by its frictional coefficient. Manning has derived an equation predicting DNA electrophoretic mobility, based on counterion condensation theory[1]. Besides universal constants, the only input parameters are the temperature, properties of the solvent such as viscosity and dielectric constant, the concentrations, conductivities and valences of the counterions and coions, and b, the charge spacing along the contour length of the polymer. The ionic strength dependence of the mobility of double-stranded DNA (dsDNA) is reasonably well predicted by this theory, using the usual b value of 1.7 Å. However, the ionic strength dependence of the mobility of unstructured single-stranded DNAs (ssDNA) is poorly predicted by the theory if the spacing between phosphate charges is assumed to be 4.0 Å or greater. If the value of b is assumed to be ~2.0 Å, only slightly greater than that of dsDNA, the ionic strength dependence of the mobility of ssDNA is well predicted by the Manning electrophoresis theory. A charge spacing of 2.0 Å for ssDNA suggests that solutions of moderate ionic strength facilitate the collapse of ssDNAs into compact unstructured conformations not dissimilar to molten globules in the protein world.

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[1] G. S. Manning (1981) *J. Phys. Chem. 85*, 1506–1615.

302-Pos Board B102

DNA Condensation at Freestanding Cationic Lipid Bilayers

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We describe a previously unreported coil-globule transition of DNA electrostatically bound to a freestanding fluid cationic lipid membrane [1]. The collapse of a DNA coil into a compact globule takes place after the DNA molecule attaches in an extended conformation to the membrane. DNA condensation is favored at a higher cationic lipid content, while at lower membrane charge densities coexistence of DNA random coils, partially collapsed conformations, and globules is observed.

[1] C. Herold, P. Schwille and E.P. Petrov, Phys. Rev. Lett. 104, 148102 (2010).

303-Pos Board B103

Transition Metal Complexes and the B-To-Z DNA Transition: The Role of Charge, Conformational Entropy and Osmotic Stress

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A combination of charge-charge interactions with the DNA backbone and site-specific hydrogen bonds to phosphates and base pairs accounts for the unusual ability of hexamminecobalt (III) and other octahedral +3 transition metal complexes to drive the B-to-Z transition. We have also observed a transition induced by +2 or +1 octahedral complexes, but at much higher concentrations. The role of water in the complex-DNA interaction has been probed by application of an osmotic stress. Circular dichroism measurements show that addition of a neutral osmolyte like sucrose shifts the equilibrium toward formation of Z-DNA, decreasing the concentration of complex required to induce the transition. The greatest osmotic sensitivity is observed with the transition driven by a +2 complex, chloropentamminecobalt (III), in which the concentration needed to reach the transition midpoint decreased 4-fold when 4.1 osmolal sucrose was used. By contrast, the transition midpoint concentration of the +3 complex hexamminecobalt (III) decreased only about 30%. The osmotic effect on a +1 complex, carbonato-tetramminecobalt (III), was of intermediate magnitude, with a two-fold decrease in midpoint concentration. We hypothesized that decreasing the donor atoms' hydrogen bonding potential through conformational constraints would make the interaction more subject to competition by waters and thus more osmotically sensitive. This was tested by comparing osmotic stress effects on the transition mediated by trisethylenediaminecobalt (III), a +3 complex with bidentate nitrogen ligands, and hexamminecobalt (III), with monodentate ligands. We observed a somewhat greater sensitivity for the bidentate complex (50% decrease in midpoint concentration) vs the monodentate complex (30% decrease). A square planar +2 complex, tetrammineplatinum (II), was unable to induce a B-to-Z transition, even when potentially competing waters were removed via osmotic stress.

304-Pos Board B104

Electric Field Control of Conformational Switching and Hybridization of Surface-Attached DNA

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Surface hybridization between end-tethered oligonucleotide ''probe'' and assayed ''target'' DNA is a key process in nucleic acid detection and analysis using DNA microarrays and microbids. Here we study how the hybridization on the surface can be controlled by applied surface potential. We developed advanced electronically controlled arrays of molecular beacon (MB) probes attached to the indium-tin oxide (ITO) surface, where the electrostatic conformational switch and hybridization with targets are investigated. The MBs are in low (high) fluorescence closed (open) state at negative (positive) potential, and undergo closed-open transition reversibly and reproducibly upon potential cycling. The switching effect is measured as a function of ionic strength, applied potential, and solution pH. At applied ± 0.8 V, 2mM [Na+] pH 9 solution, $10 \pm 4\%$ MBs are electrostatically switchable; the extent of switching decreases at higher ionic strength, lower surface potential, and neutral pH. Interestingly, the sign of switching is opposite to an expectation that the repulsion (attraction) from surface opens (closes) end-tethered MB; it can be understood as a result of electrostatic interaction between MBs and charged surface, if substantial condensed counterions release from MBs is taken into account.

Our central result is finding of the strong electric field effect on hybridization of surface-attached MBs with assayed DNA targets. The hybridization is enhanced by applied positive potential, whereas the MB-target duplexes denature at negative potential. The relative effect on the extent of hybridization increases at low target concentration and achieves denaturation of 90% of hybrids by surface potential −0.8 V. Our results are accurately described by developed theoretical isotherm for hybridization of DNA arrays with electrified surface. Demonstrated strong and simple control of the surface hybridization by applied potential is of interest for advanced electronic DNA hybridization technologies like microarrays and solid-phase PCR.